Supercollisions and energy transfer of highly vibrationally excited molecules

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Collisional energy-transfer probability distribution functions of highly vibrationally excited molecules and the existence of supercollisions remain as the outstanding questions in the field of intermolecular energy transfer. In this investigation, collisional interactions between ground state Kr atoms and highly vibrationally excited azulene molecules (4.66 eV internal energy) were examined at a collision energy of 410 cm^{-1} using a crossed molecular beam apparatus and time-sliced ion imaging techniques. A large amount of energy transfer (1000–5000 cm^{-1}) in the backward direction was observed. We report the experimental measurement for the shape of the energy-transfer probability distribution function along with a direct observation of supercollisions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2062167]

Lindemann[1] was the first to acknowledge the importance of collisional energy transfer in the excitation and deexcitation processes in thermal unimolecular reactions. Lindemann's simple formulation for gas-phase unimolecular reactions involves a sequence of three elementary steps, i.e., activation, deactivation, and reaction. The three-step mechanism gives a pressure-dependent expression for the unimolecular rate constants in thermal systems.

The derivation of these rate constants from the Lindemann mechanism is based on the explicit assumption that collisions are strong or efficient enough to maintain the equilibrium Boltzmann distribution of reactants. For strong collisions the energy transfer is generally assumed to be large. If collisional encounters are inefficient in transporting molecules up and down the energy ladder, the equilibrium Boltzmann distribution will not be maintained and experimental rate constants will deviate from predicted values. Studies concerning the pressure dependence of unimolecular reaction rates have revealed that most collisions are far less efficient than strong collisions.[2–4]

Recently, Oref *et al.* conducted experiments in which energy transfer was monitored by employing a bath gas that could undergo a unimolecular reaction. An extraordinary large amount of energy transfer from a single collision was observed.[5–7] The following classical trajectory calculations discovered that a small fraction of collisions do transfer inordinate amounts of energy. Simulated collisional energy-transfer probability distribution functions $P(E',E)$ from selected initial energy E to final energy E' states exhibited a tail at high energies.[8,9] These large energy changing ΔE collisional encounters, observed from experiments and calculations, are called "supercollisions." Although their probabilities are much smaller than those assumed by the strong-collision model of unimolecular reaction rate theory, supercollisions have been shown to influence chemical reaction rates. For example, at 1500 K, simulation showed that unimolecular rate constants were found to change by factors of 3 and 11 for 0.1% and 0.5% supercollisions, respectively.[10]

It has been suggested that without reliable energy-transfer probability distribution functions $P(E',E)$, little progress can be made in understanding the dynamics of energy transfer.[2–4] Unfortunately, the energy-transfer probability distribution function still remains extremely hard to measure experimentally or to calculate theoretically. Thus far, most experiments have yielded averaged quantities, such as the first moment $\langle \Delta E \rangle$ (i.e., the mean energy lost per collision) and the second moment $\langle \Delta E^2 \rangle$ of $P(E',E)$. Recent experiments utilizing spectroscopic methods have provided greater insight into the shape of the function. Unfortunately, in these experiments, an empirical distribution function must be chosen in order to fit the experimental data.[11,12] Additionally, extensive averaging over multiple collisions, thermal velocity, and population distributions obscures much of the details. As a result, the energy-transfer probability distribution function has yet to be directly observed. It is therefore possible that the classically simulated "tail" and the experimental phenomenon of supercollisions are unrelated. To better understand the nature of energy-transfer reactions, experiments are needed both to evaluate $P(E',E)$ as a function of ΔE and to identify the contribution of supercollisions to such processes.

In this work we examine the energy-transfer dynamics of highly vibrationally excited azulene (Az) using a crossed molecular beam apparatus in conjunction with time-sliced ion imaging techniques. We report the first experimental measurement of the shape of $P(E',E)$ along with a direct observation of supercollisions. Briefly, Az molecules in a

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molecular beam were excited to the S_4 state by 266 nm photons. Highly vibrationally excited or "hot" Az having an internal energy of 4.66 eV was produced via rapid internal conversion to the ground electronic state. Because Az has a very large absorption cross section at 266 nm, we readily saturated the absorption, thus generating large amounts of hot Az in the molecular beam. The relative concentrations of the cold Az and the highly vibrationally excited Az in the molecular beam were measured using a time-of-flight mass spectrometer and vacuum ultraviolet (VUV) photoionization at 157 and 118 nm.[13] As much as 73% of the Az molecules absorbed only a single 266 nm photon and became hot Az 19% of Az molecules absorbed two or more ultraviolet (UV) photons. They either isomerize to naphthalene and dissociate into fragments within a few nanoseconds,[14] or become cations. Fragments had no effect on the experiment because we only probed parent mass. These Az cations were repelled out of the molecular beam by an electric field. As little as 8% of the Az molecules did not absorb any UV photons and remained as cold Az.

The hot Az molecular beam was then crossed with a ground state Kr atom beam. Based on the principle of conservation of momentum, the shape of the energy-transfer probability distribution function was obtained from a measurement of the scattered Az velocity distribution in the center-of-mass frame. Scattered Az molecules were photoionized by a 10-mm-wide pulsed laser sheet at 157 nm. Translational energies for the angular-resolved scattered Az molecules were measured using time-sliced velocity map ion imaging techniques.[15,16] The VUV ionization laser crossed a large ionization area in order to minimize the experimental uncertainty in the density-to-flux transformation.[16] A weak extraction field was applied to the ion optics to keep the velocity resolution at 2.3% even if the ions were collected from a large ionization volume.[15] Because there is a lot of unscattered Az in the molecular beam, the 157 nm laser beam will also ionize these molecules and generate a large amount of ions. These ions have nearly the same velocity (molecular beam velocity) and can easily be focused by the ion optics into a small spot on the multichannel plate (MCP) detector. In order to avoid saturating and even possibly damaging the detector, a 2 mm$\times$25 mm stainless steel pin (located 5 cm in front of the MCP detector) was used to block these ions. Most of the scattered Az having velocities different from that of the molecular beam was not affected by the stainless steel pin.

Figure 1 shows the image for scattered Az from collisions of hot Az molecules with ground state Kr atoms at a collision energy of 0.051 eV(410 cm^{-1}). The intensity resulting from the small portion of scattered cold Az in the molecular beam has been subtracted from this image. The rectangular blank located in the upper right-hand corner is the part of the image that was blocked by the stainless steel pin, which was positioned in front of the MCP detector. The elastic collisions are distributed along the elastic collision circle according to their deflection angles. The elastic collisions that have small deflection angles are obscured by the stainless pin and cannot be detected. The image inside of the elastic collision circle of the Newton diagram represents the

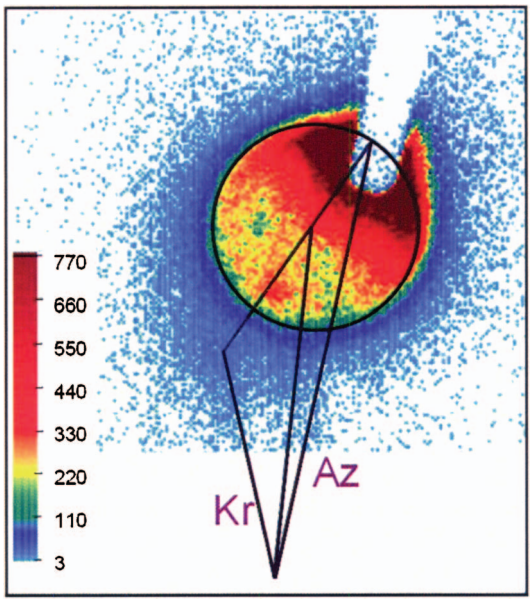

FIG. 1. (Color) Image of scattered hot azulene (4.66 eV internal energy) and the Newton diagram. The collision energy is 0.051 eV. The circle represents elastic collisions.

energy up (ΔE_{up}) translation to vibration/rotation (T-V/R) collisions, whereas the image outside of the circle represents the energy down (ΔE_{down}) vibration to translation (V-T) collisions. The image has large intensities at the forward direction on the circle of elastic collision as well as inside the circle. Additionally, there is a weak backward peak inside the elastic collision circle. Observation of a strong forward scat-

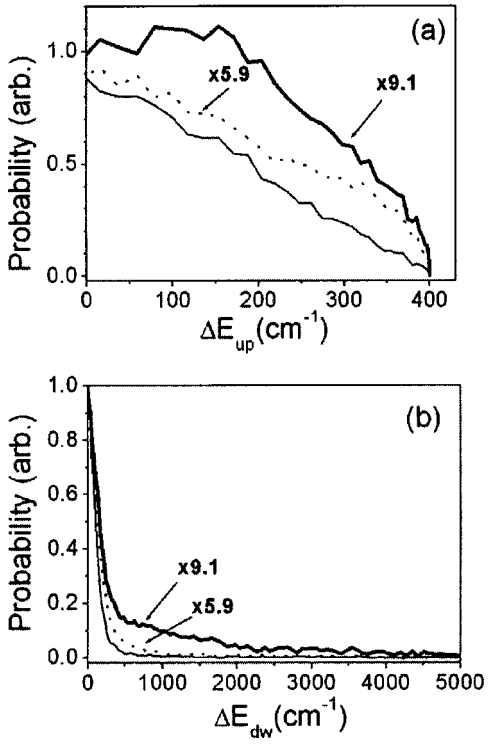

FIG. 2. Energy-transfer probability distribution functions for various scattering angles: forward scattering (30°–40°, thin solid line), sideway scattering (80°–100°, dotted line), and backward scattering (160°–180°, thick solid line). (a) Energy up collisions; (b) energy down collisions.

tering peak along with a weak backward scattering peak indicates the formation of a short-lived Az-Kr complex. The complex resulted in small amounts of ΔE_{up} transfer. Outside of the elastic collision circle, forward scattering has a relatively large intensity for small amounts of energy transfer. As ΔE_{down} increases, the intensity in the forward direction rapidly decreases. However, a tail remains for large ΔE_{down} in the backward direction.

Energy-transfer probability distribution functions for various scattering angles are illustrated in Fig. 2. The energy-transfer probabilities for both energy up *T-V/R* and energy down *V-T* collisions are shown. For energy up collisions, it is dominated by forward scattering. The small rise of the energy-transfer probability distribution for backward scattering as the ΔE_{up} increases is mainly due to the backward peak, resulting from the formation of the Az-Kr complex. On the other hand, the shapes of the distributions for energy down collisions are nearly the same for forward and sideway scattering. Most of the energy transfer for these processes is less than 500 cm^{-1}. However, the energy-transfer probability distribution in the backward scattering direction features a high-energy tail and energy transfers as large as 1000–5000 cm^{-1} are observed.

The total energy-transfer probability distribution function was obtained directly from a summation of the energy-transfer probability distribution functions at various scattering angles. Since a small portion of the image at forward direction was obscured by the stainless pin, the image intensities in these regions were obtained via extrapolation from the values at larger scattering angles. The final total energy-transfer probability distribution function is shown in Fig. 3. The collision energy is fixed at 410 cm^{-1}(0.051 eV) and

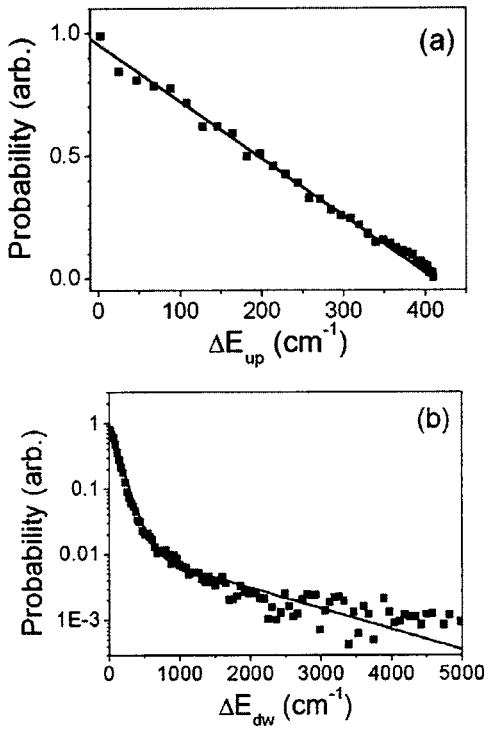

FIG. 3. The shape of the total energy-transfer probability distribution function (integrating over all scattering angles). (a) Energy up collisions; (b) energy down collisions.

therefore the maximum value for ΔE_{up} is 410 cm^{-1}. The energy up distribution function can be best approximated by a linear function, $0.955-0.00233\times\Delta E_{up}$. The maximum transferred energy reaches the maximum available energy, which shows that a large fraction of the translational energy can be transferred to vibrational energy. By contrast, the maximum transferred energy in energy down collisions does not reach the maximum available energy. Only a small fraction of the vibrational energy was transferred to translational energy. The probabilities for energy down collisions decrease rapidly with increasing ΔE_{down}. However, there is a tail at large ΔE_{down}. The shape of the total energy-transfer probability distribution function (integrating over all scattering angles) may best be described using a biexponential function, $\exp(-\Delta E_{down}/120)+0.013\times\exp(-\Delta E_{down}/1400)$. The average energy transfer for the first exponential function is 120 cm^{-1}, whereas the average energy transfer for the second exponential function is 1400 cm^{-1} (nearly 12 times larger). The main contribution to the second exponential function comes from the tail at large ΔE_{down} in the backward scattering direction. Large energy transfers, observed only in the backward scattering direction, suggest that a different energy-transfer mechanism is in operation. This particular type of collision must be a supercollision. Note that only the shape of the energy-transfer probability distribution function is given here. No absolute collision cross section can be obtained due to the difficulties in calibrating the absolute molecular beam intensities and crossing volume.

Classical trajectory calculations have been employed to evaluate collisions between highly vibrationally excited molecules and rare gases.[9,17,18] Small numbers of collisions transferring large amounts of energy is the observation. Some of the collisions were found to have an energy-transfer mechanism different from that of "normal" energy transfer. They are dynamically constrained. The probability for supercollisions is about 2–3 orders of magnitude smaller than that for a small energy transfer. The supercollisions that we observe are solely in the backward scattering direction, which indicates that these collisions occur at small impact parameters. The probability for supercollisions, defined arbitrarily as the scattered Az in the region $160°<\theta<180°$ and $\Delta E_{down}>2000$ cm^{-1}, is about 1% of the total collision probability. The average energy transfer for supercollisions is about $\langle\Delta E_{sup}\rangle=3156$ cm^{-1}. This is large when compared to the average transferred energy: $\langle\Delta E_{down}\rangle=267$ cm^{-1}. The amount of energy transferred due to supercollisions ($\langle\Delta E_{sup}\rangle\times 1\%$) is about 11% of the average transferred energy in energy down collisions, indicating that the effect from supercollisions is not a minor one. The effect of supercollisions on other properties, such as reaction rates, which depend nonlinearly on the amount of energy transferred, should be even larger than that for the average energy transferred.[18]

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